CO_2 Capture Process Using Phase-Changing Absorbents

GE Global Research
GE Energy
University of Pittsburgh

ARPA-E Contract: DE-AR0000084

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Team Members

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Program Summary

Program Team

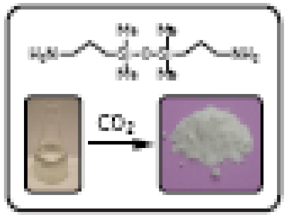
GE Global Research
- Material Development
- Unit Op Design/Testing

GE Energy
- Modeling, and Design of Integrated Energy Systems
- Economic Analysis

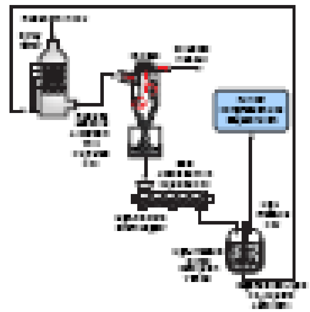
University of Pittsburgh
- Absorption Testing of Materials
- Property Measurement

CO_2 Capture Process Using Innovative Phase-Changing Absorbents, 2 -Year, \$3.8M

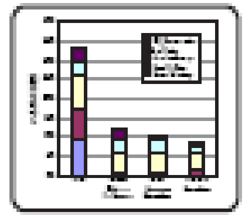
Program Objective: *To develop a cost-efficient process that utilizes a CO_2-capture absorbent that reversibly transforms from a liquid to a solid upon reaction with CO_2 to remove CO_2 from flue gas derived from pulverized coal fired power*



Material Advancement



Process Development



Plant and Process Modeling

Technical Approach

- Optimized advanced phase-changing absorbent
- Design innovative process integration absorption of CO_2, transfer of solid material, and desorption of CO_2 under pressure
- Develop and optimize plant and process modeling for unique CO_2 capture process

Program Deliverables

- A material and CO_2 absorption/desorption process that results in <10% parasitic power load and <\$25/ton of CO_2 captured

Anticipated Benefits of the Proposed Technology

- Eliminate 1 billion tons of CO_2 emissions from PC power plants
- Increase energy security with market for domestic coal
- U.S. leads CO_2 capture technology
- Increase energy efficiency for CO_2 capture vs. MEA
- Create jobs in construction and manufacturing

- Develop cost-efficient process utilizing a phase-changing sorbent
- Build off of prior DOE/NETL program using amino-silicones

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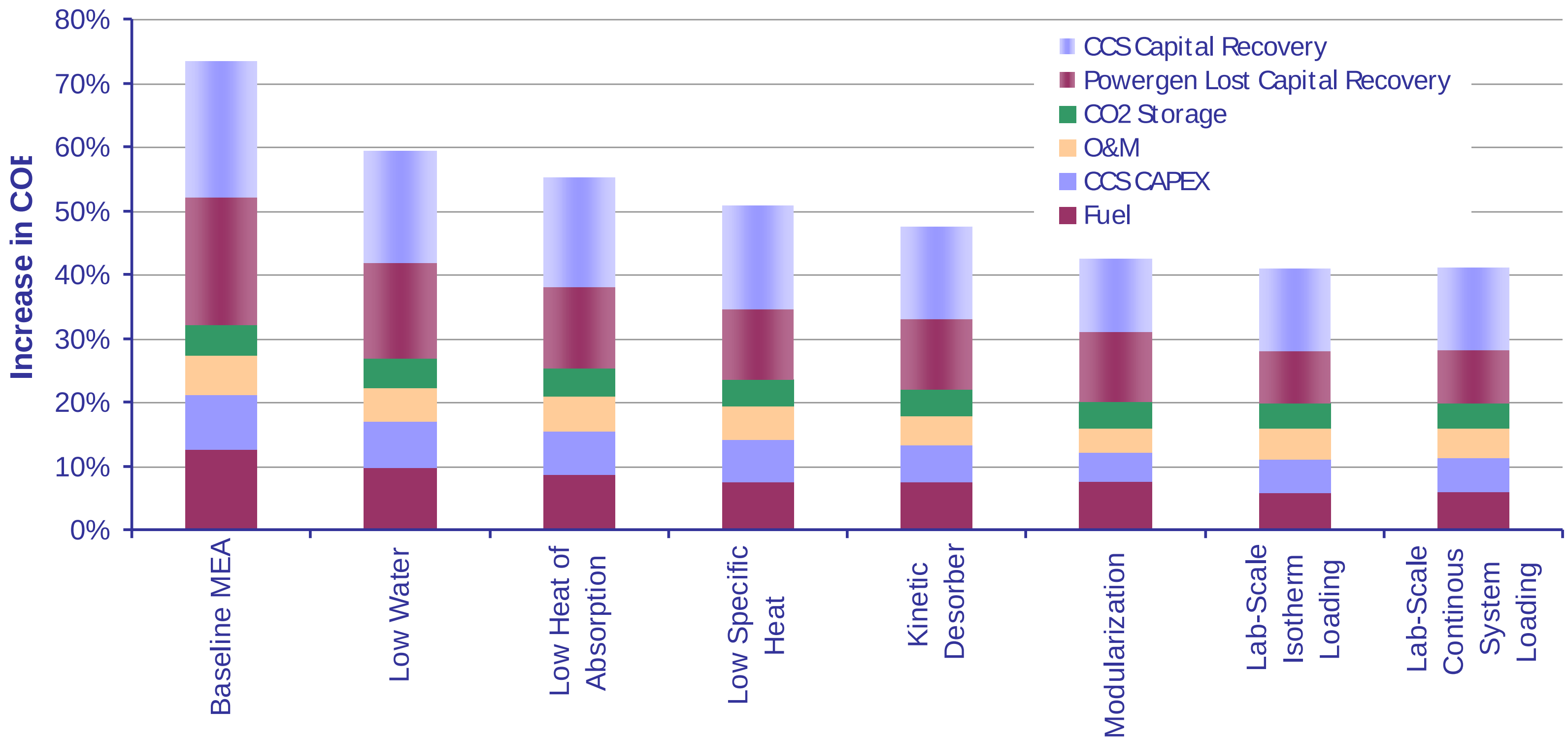
Increase in COE over Non-Capture Case for prior NETL Project



- GAP-1/TEG system

R. Vipperla

- Significant benefit with low water system
- Additional advantage with lower ΔH_{rxn} and C_p
- Calculated 41% increase in COE vs 74% for optimized MEA system

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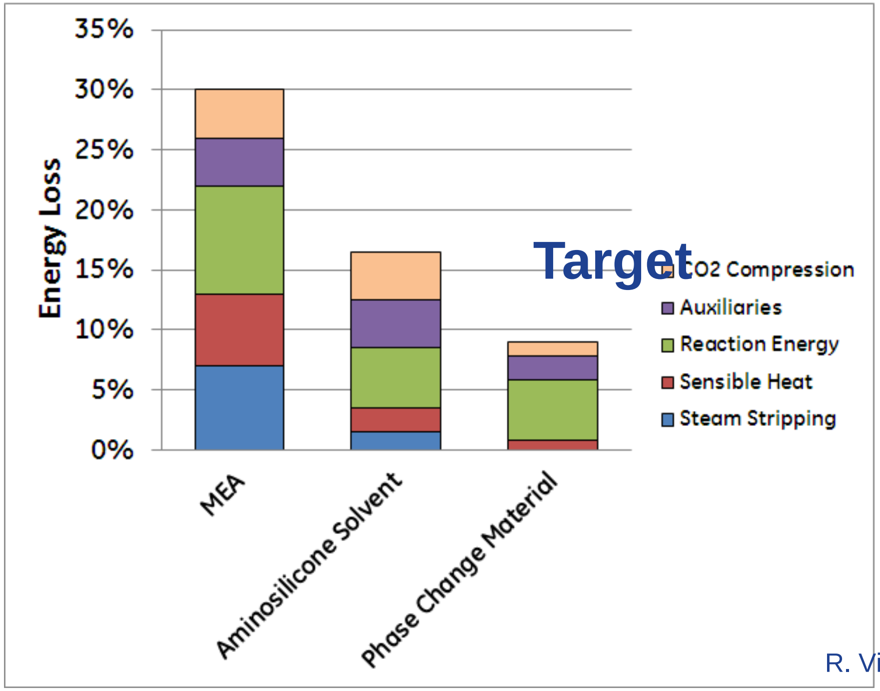
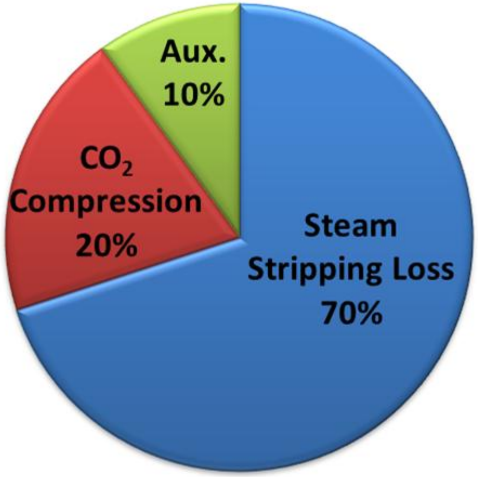
ARPA-E Phase Change (Driver – Economics)



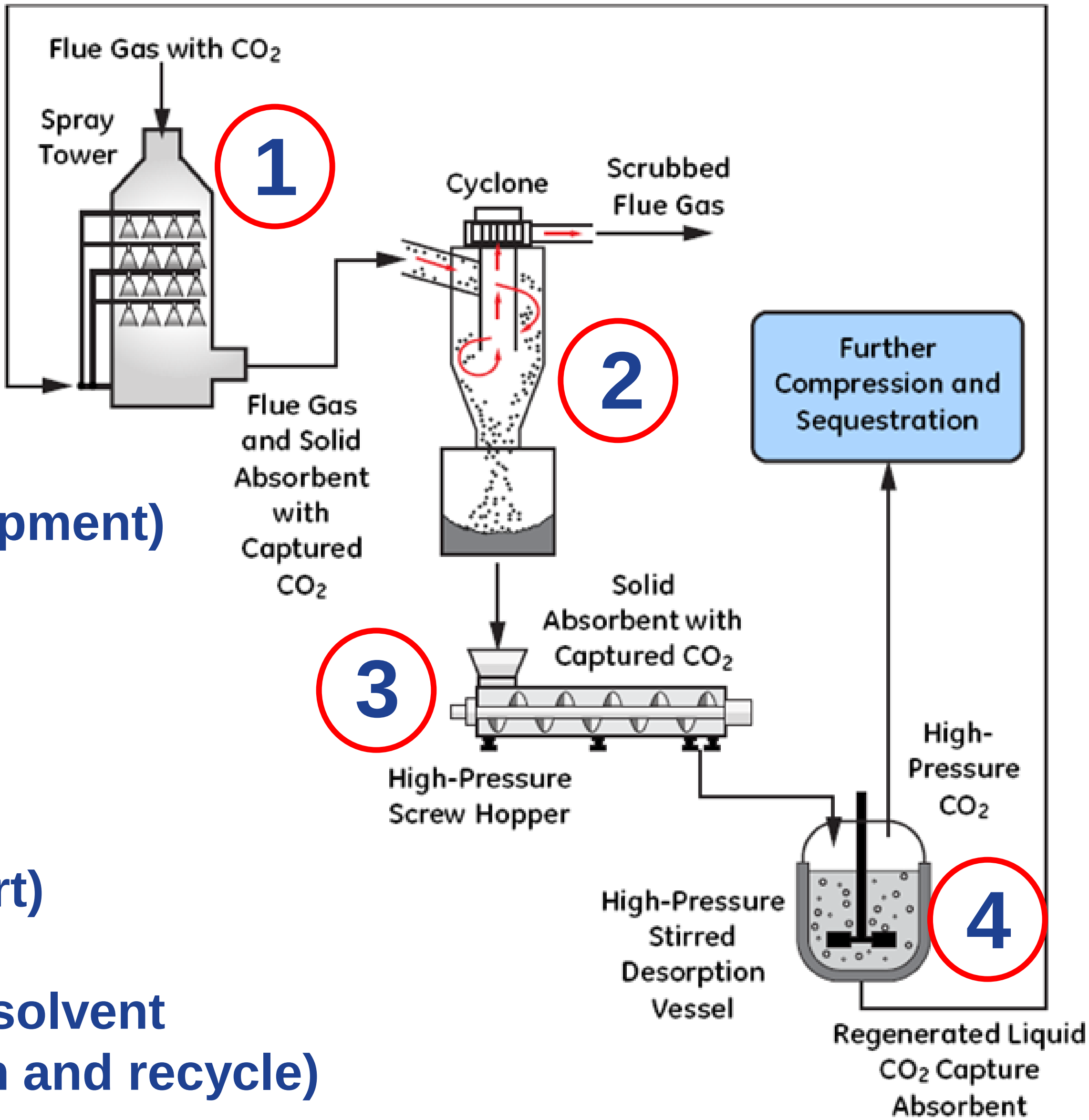
R. Vipperla

Conventional Solvent Systems



- 30% power lost in conventional MEA process (70-80% increase in COE)
- Significant portion of that due to heating/condensing water
- Low water based processes reduce energy/cost (~40% COE increase)
- Eliminate all non-reactive co-solvents (potential of ~30% COE increase)

Phase Change Concept



1 **Make the solid (Solvent development)**

2 **Collect the solid (Solid isolation)**

3 **Move the solid (Solids transport)**

4 **Regenerate the solvent (CO_2 desorption and recycle)**

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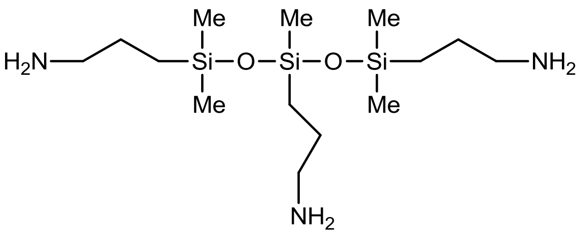
Solvent Development

- Primary amines rapidly react with CO_2 to form carbamate salts

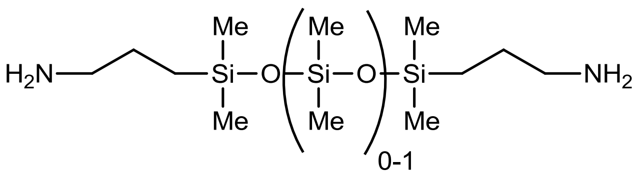
$$2\ R{-}NH_2 + CO_2 \underset{\Delta}{\rightleftharpoons} R{-}NH_3^{\oplus} + R{-}NHCO_2^{\ominus}$$

- Systematically vary chemistry and structure for optimal reactivity
- Representative materials found that:
  - are low viscosity liquids
  - produce solids on exposure to CO_2
  - have high CO_2 uptake
  - thermally reversible



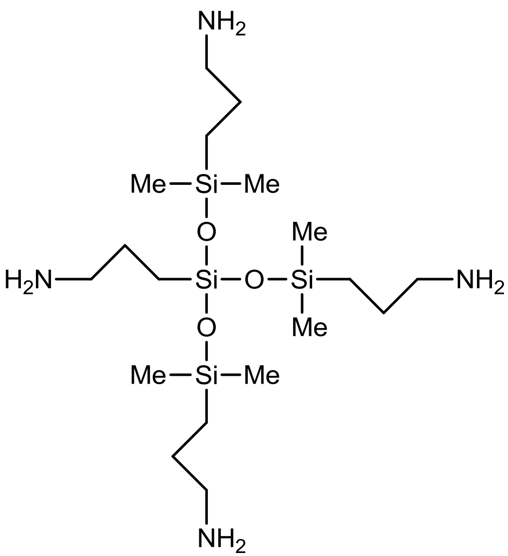
M’D’M’

17.8 % CO_2 uptake



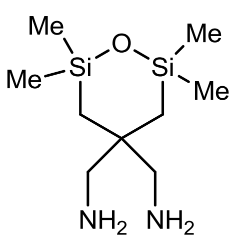
GAP-0/1

13.1 - 17.3% CO_2 uptake



M’$_3$T’

18.8 % CO_2 uptake



cyclic

15.5 % CO_2 uptake

Solvent Development

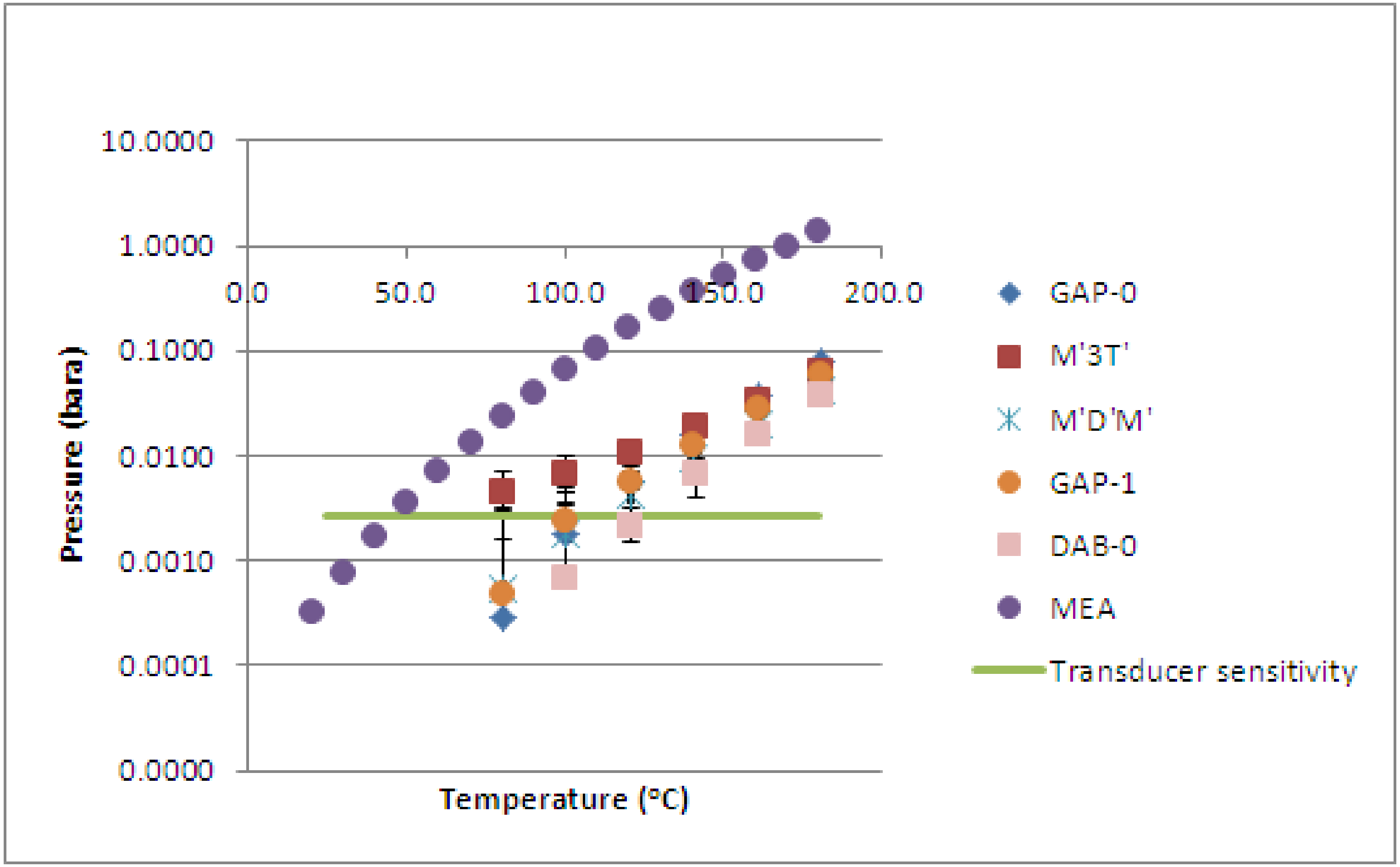
- Powder formation with dry CO_2
- Flue gas contains water
- What happens with wet CO_2?

	Dry CO_2			Wet CO_2			
Absorbant	**% Wt Gain**	**% of Theoretical**	**Salt Form**	**% Wt Gain**	**% of Theoretical**	**Salt Form**	**% of Dry**
GAP-0	17.3	98	Powder	18.4	104	Chunky Solid	106
GAP-1	13.1	96	Powder	14.1	103	Sticky Wax	108
M'D'M'	17.8	99	Powder	16.6	92	Glass	93
M'3T'	18.8	103	Powder	17.4	95.5	Sticky Gum	93
Cyclic Diamine	15.5	82	Powder	20.7	109	Powder	134

M. O'Brien

- 3 materials maintain solid form with saturated CO_2
- No loss of capture capacity
- Scaling up materials for spray drying

Vapor Pressure



R. Farnum, T. Perry, S. Genovese

- All aminosilicone materials tested exhibited vapor pressures < MEA

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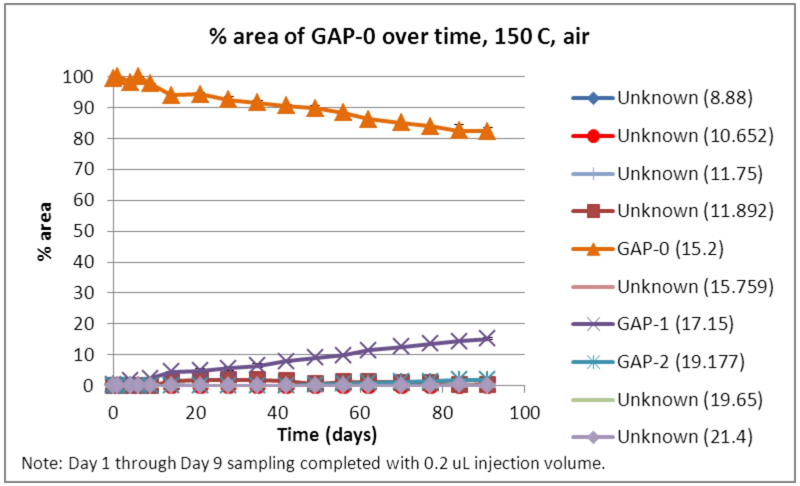
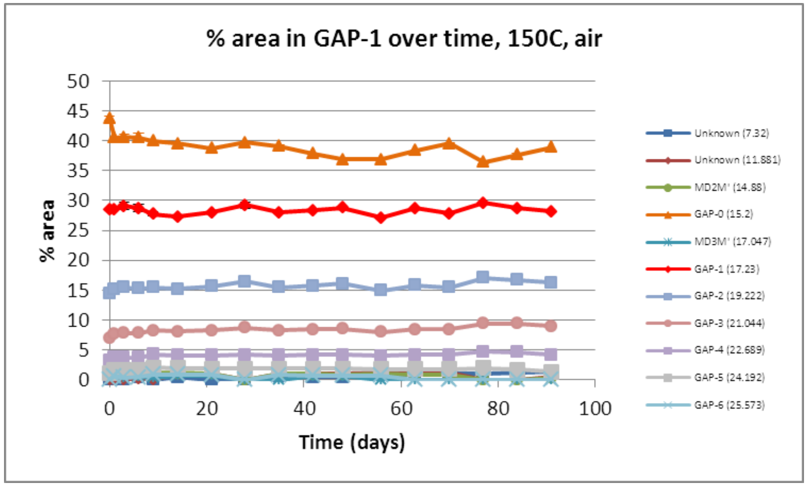
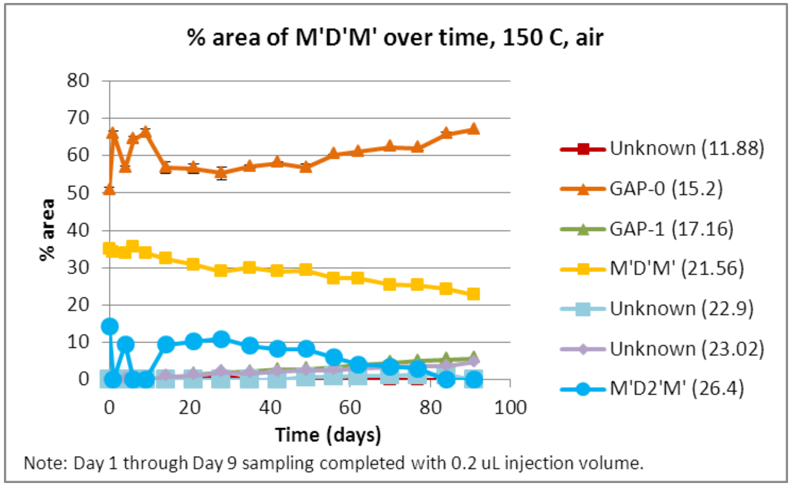
Thermal Stability



Note: Day 1 through Day 9 sampling completed with 0.2 uL injection volume.



R. Farnum



Note: Day 1 through Day 9 sampling completed with 0.2 uL injection volume.

- Excellent thermal stability
- Major decomposition products are higher homologues
- On-going experiments with stabilizers

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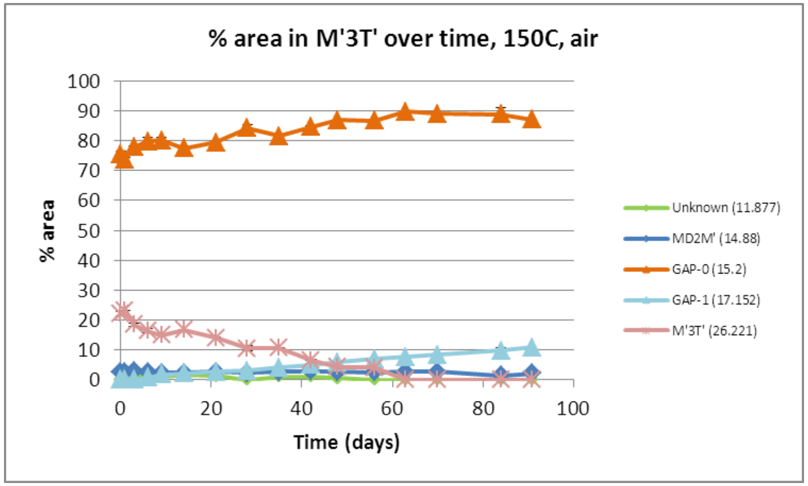
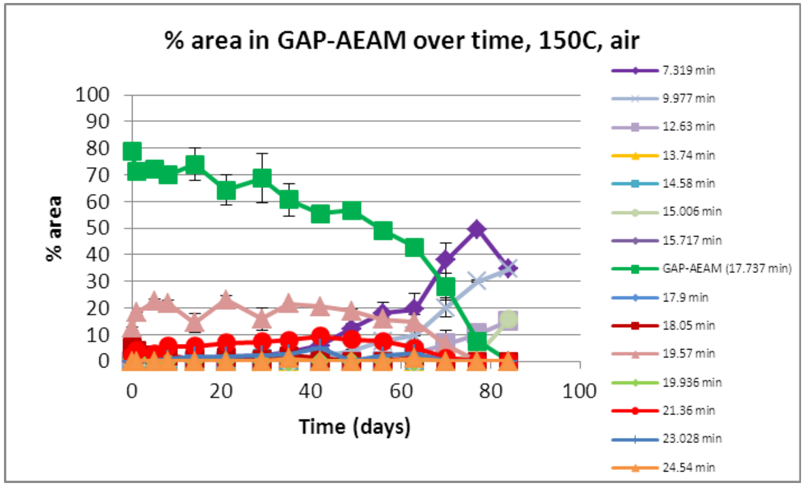
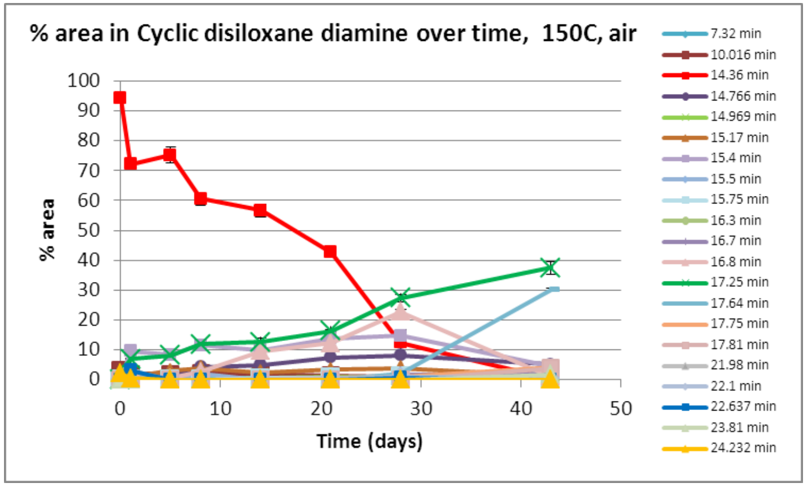
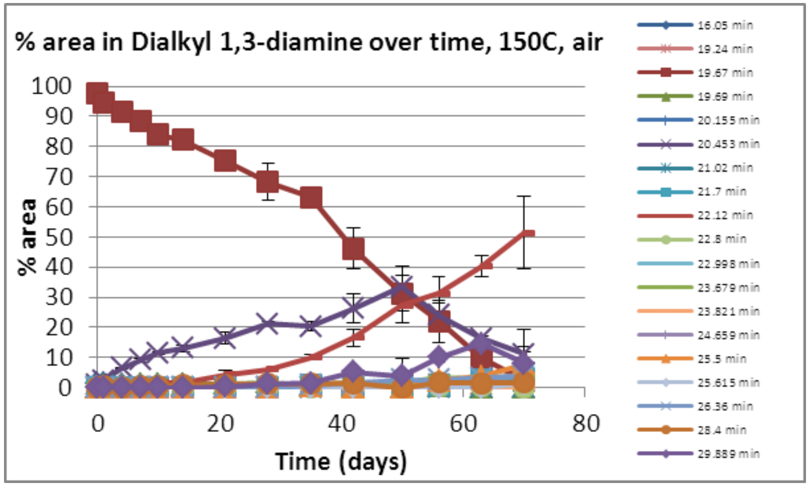
Thermal Stability





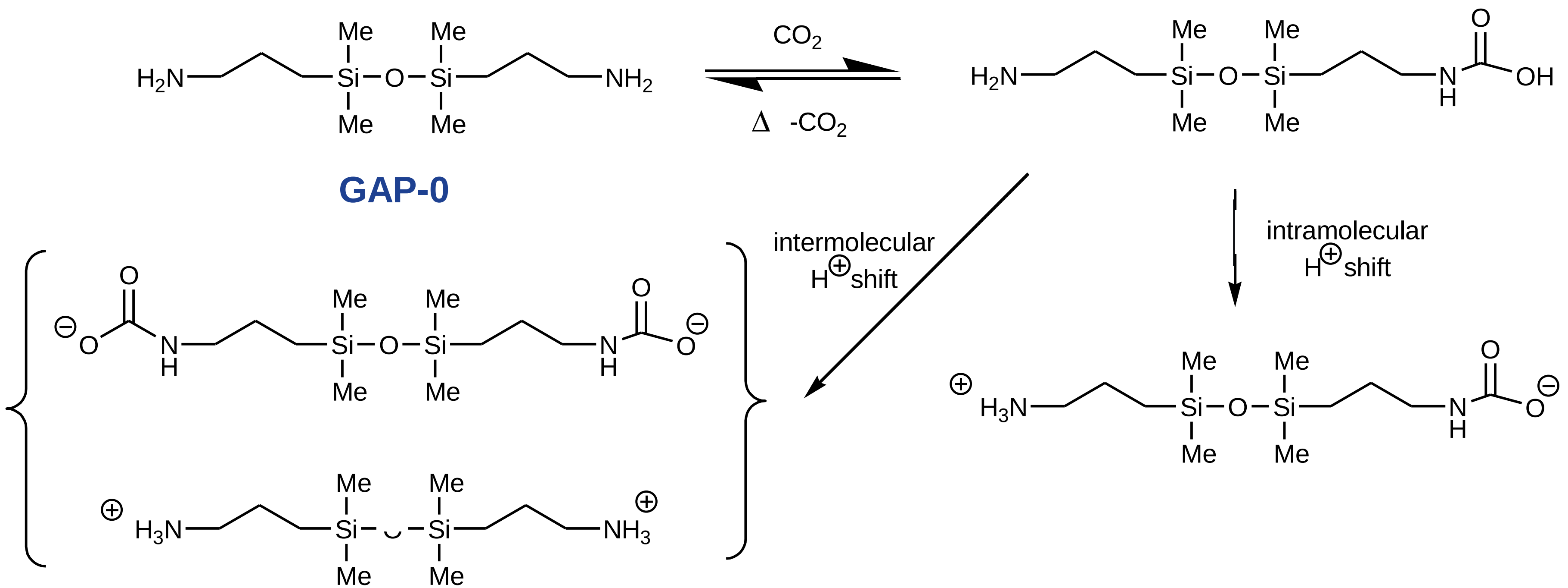




R. Farnum

- Demonstrated poor thermal stability

Carbamate Salt Formation



- GAP-0 chosen as GEN 1 solvent
- Acceptable CO_2 loading
- High boiling point
- Reversibility
- Fast reaction rate
- Thermal stability

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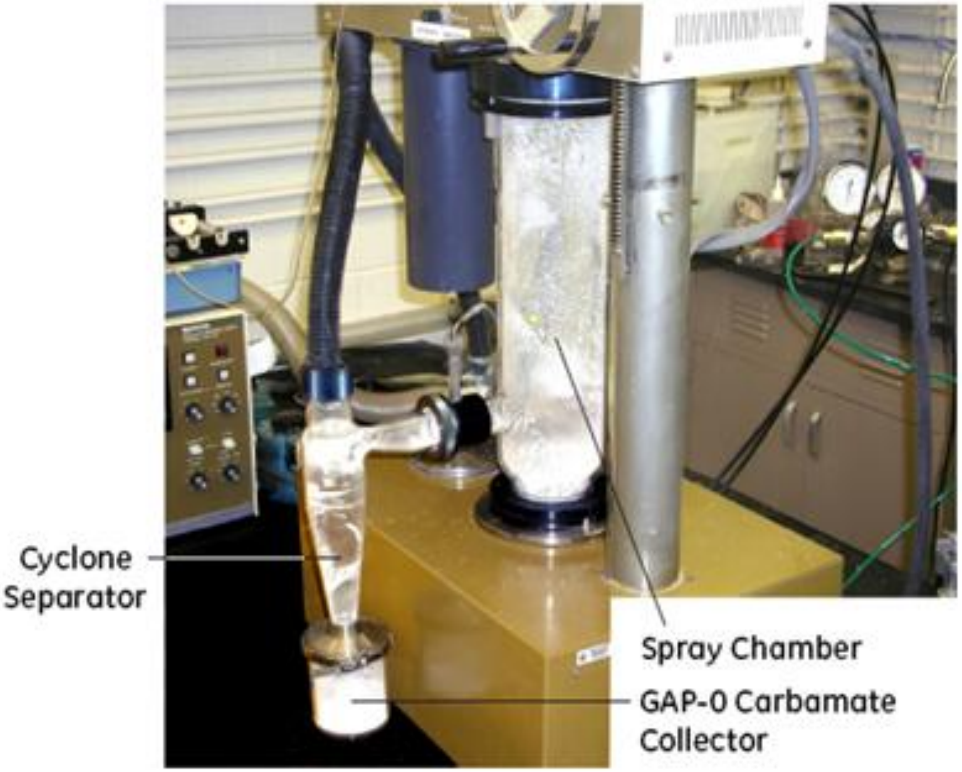
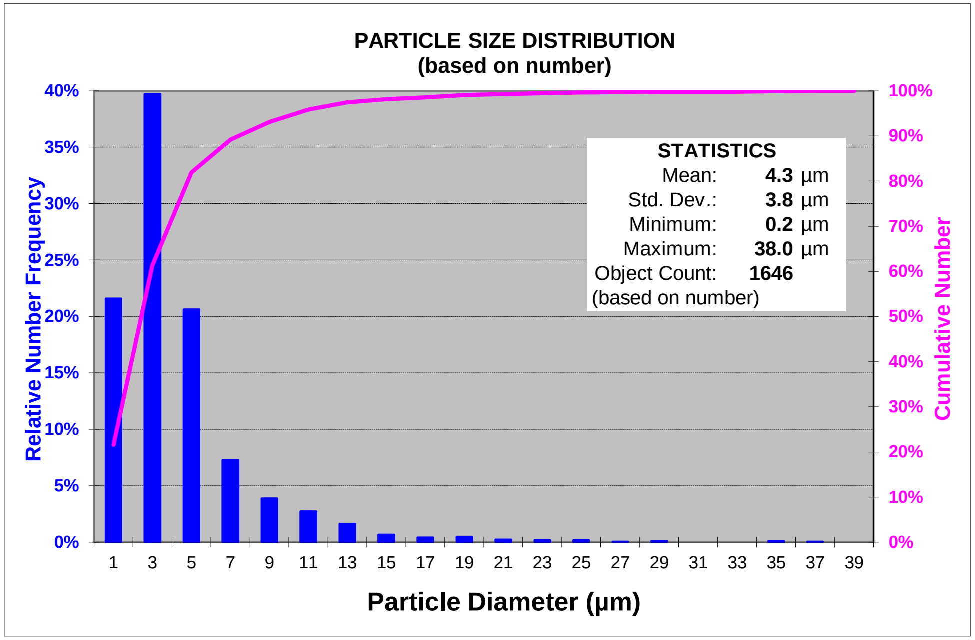
Solid Formation and Isolation

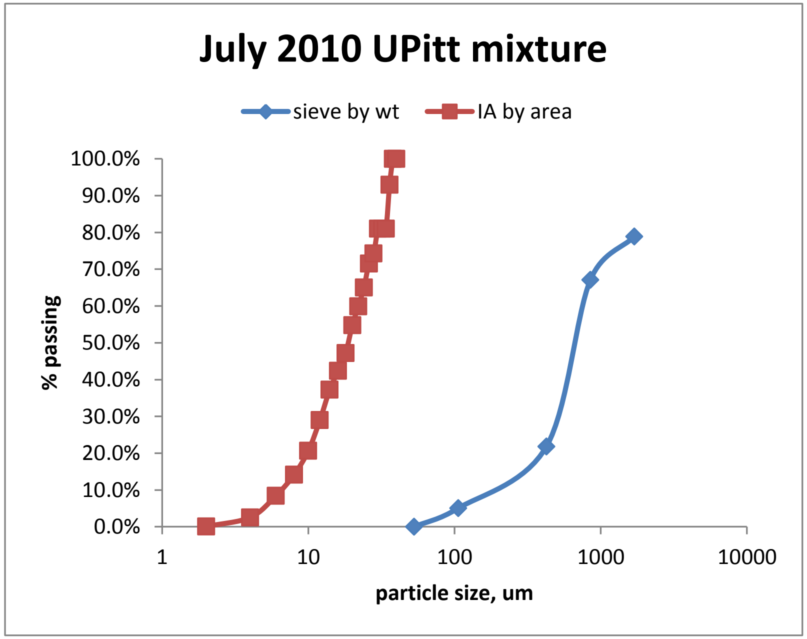


B. Enick
D. Tapriyal
L. Hong

- Spray drier with co-current CO_2 flow
- Nearly instantaneous solid formation
- 50-100 g sample size
- Additional instrument procured

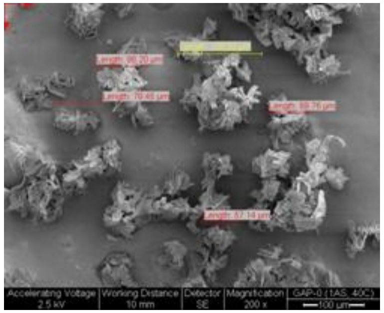
PSD by Image Analysis





Mean size = 4.3 um
Aspect ratio 0.6-1.0 (most 0.75-0.9)

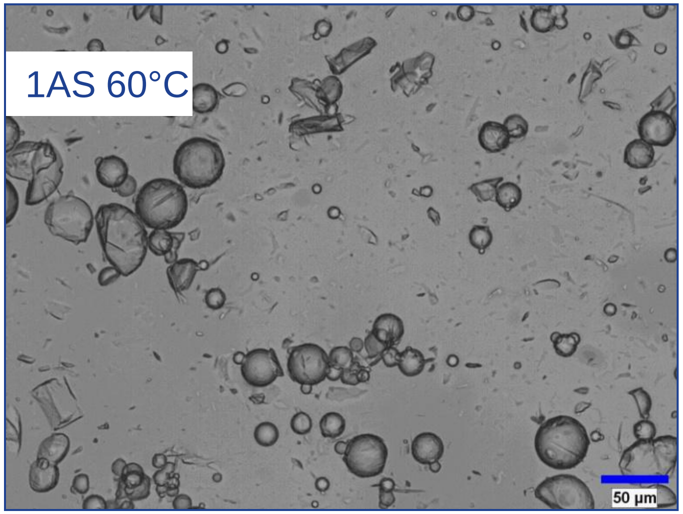
Sieve measures agglomerate size (as expected)

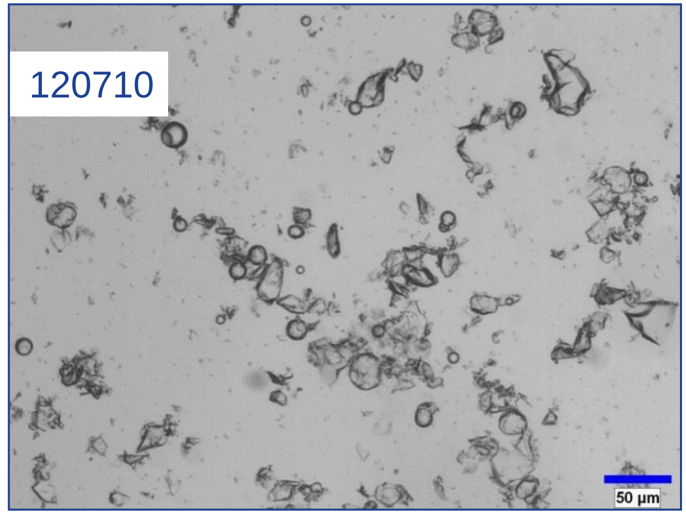


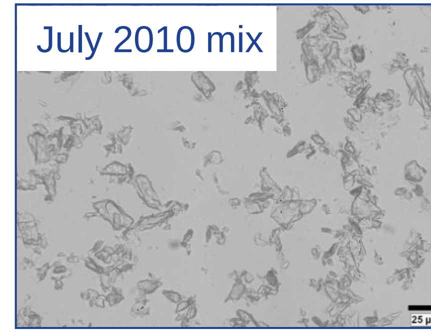
- For solids handling want ~ 500 μm particle size
- Need much larger particles

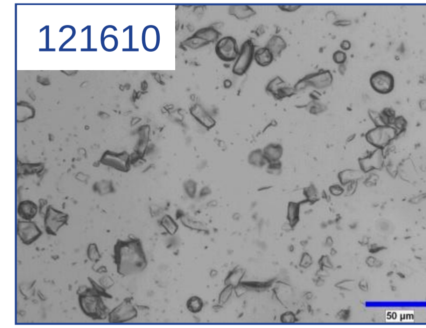
Sample images

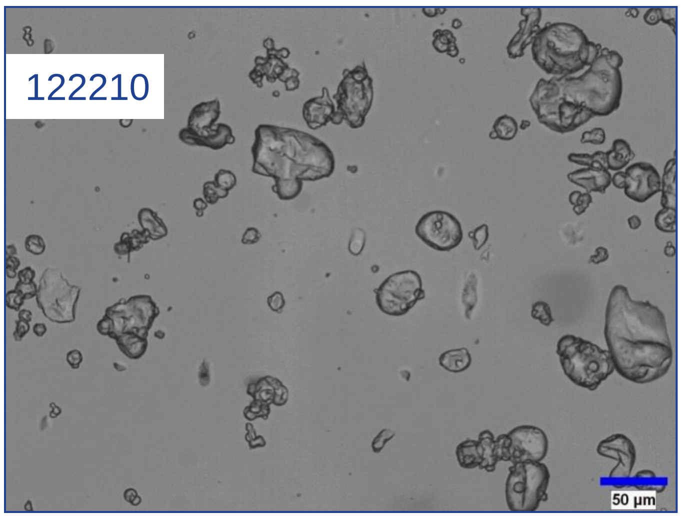
Images are on the same scale

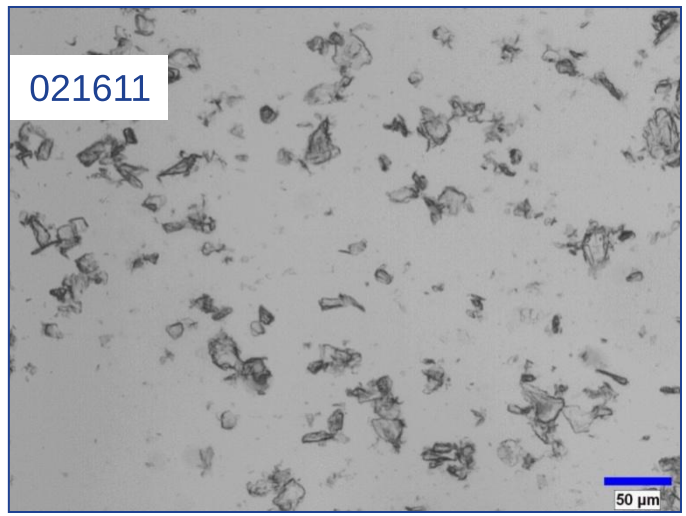


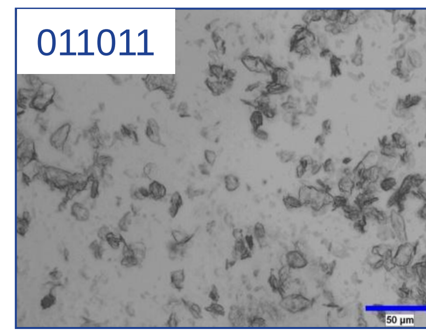


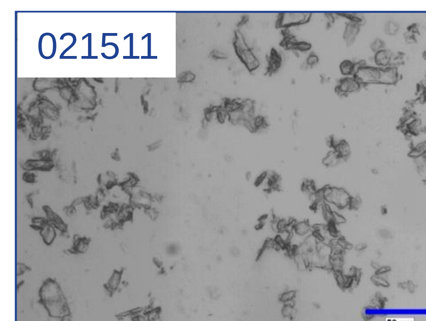






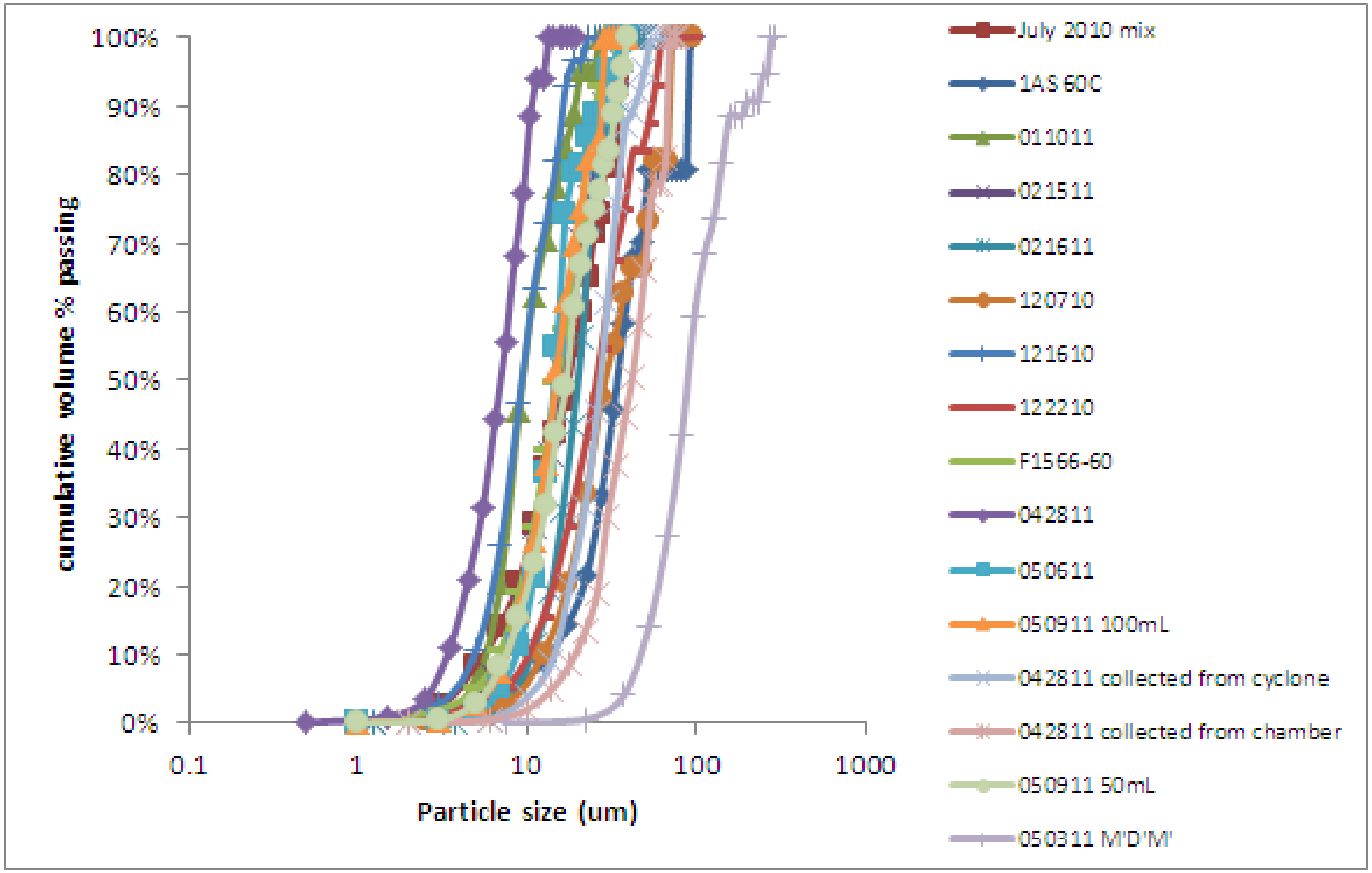






- All particles are ~ same size
- Mean size <50 μm

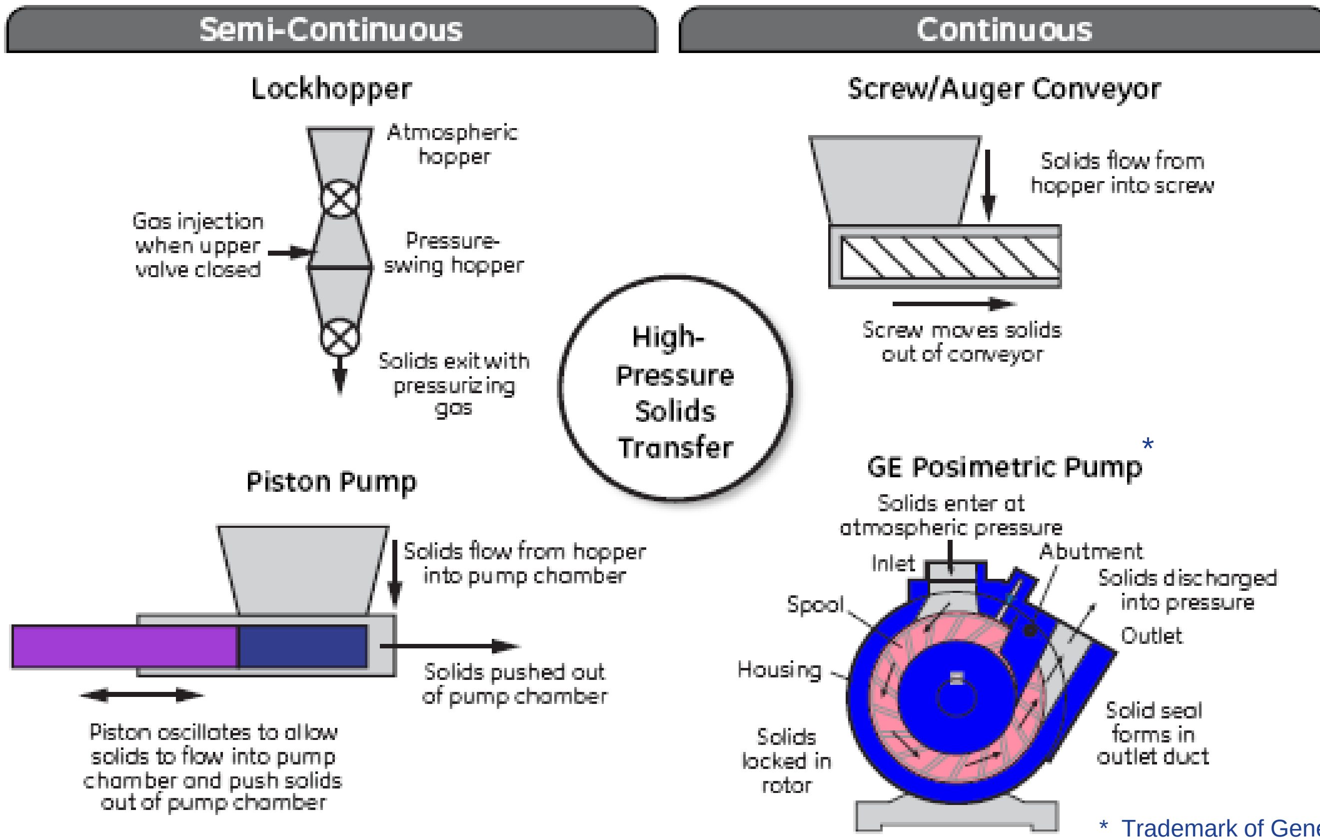
Image Analysis



- Confirmation of particle size similarity
- Mean size <50 μm
- Single exception of M'D'M'

T. Westendorf
J. Grande

Options for solid transport



* Trademark of General Electric Company

- contingent upon physical characteristics of solid
- density, shape , cohesiveness, moisture content, thermal stability
- integration between absorber and desorber
- low pressure to high pressure

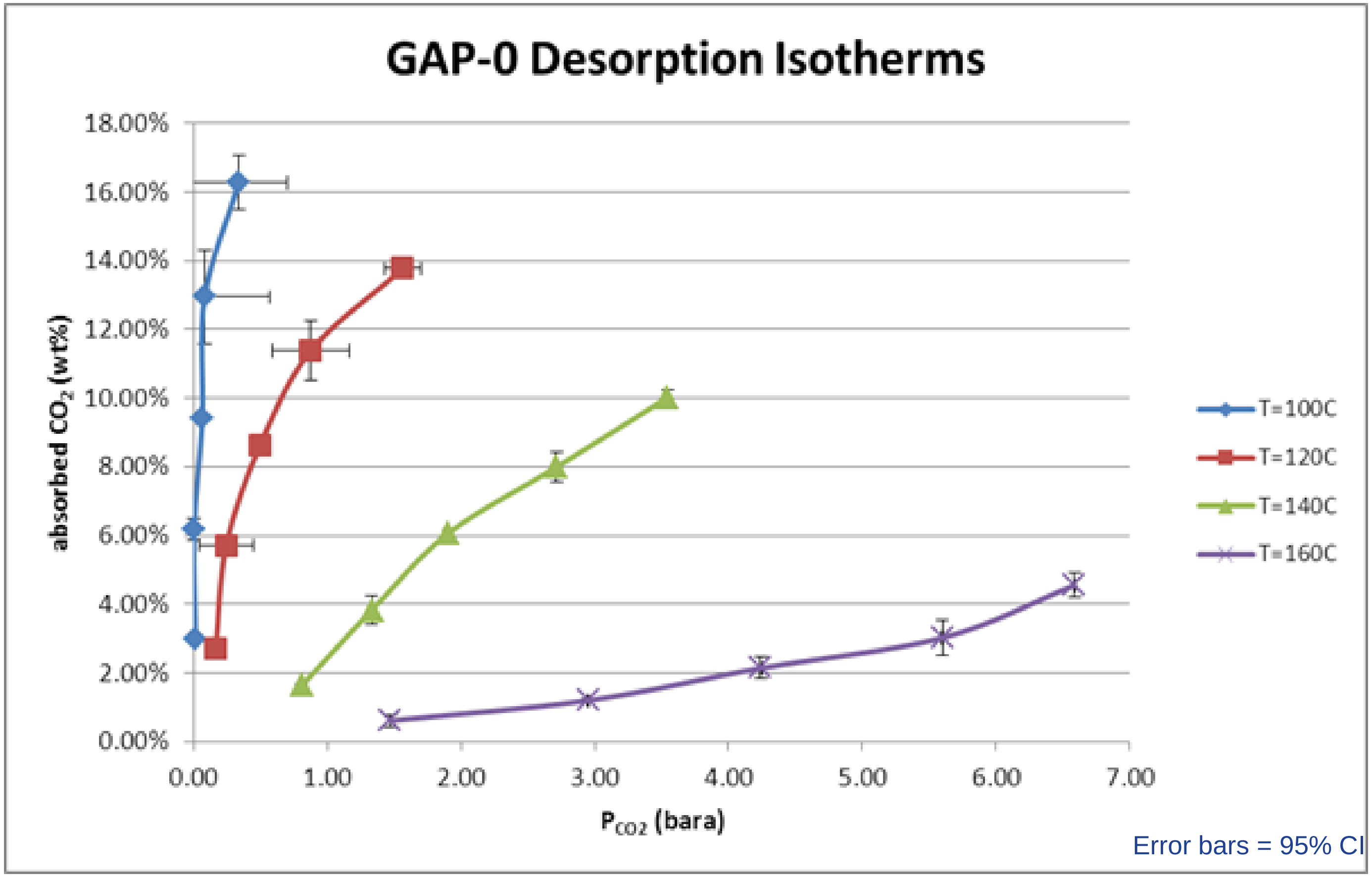
T. Westendorf

Dry Solids Transfer

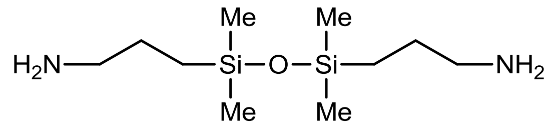
	Posimetric Pump	Screw Conveyer	Lockhopper	Piston Pump
Batch/continuous	Continuous	Continuous	Semi-continuous	Semi-continuous
Charge cycle	Hopper flow of freely-flowable solids into unit			
Pressure seal	Compressed solids plug	Compressed solids extruded through die at barrel exit	Pressure swing chamber isolation valves	Solids compressed in piston chamber
Solids discharge	Mechanical rotation of pump spool	Mechanical rotation of screw	Hopper flow, assisted by pressurized gas	Mechanical discharge
Advantages	Designed for low wear	Heat exchange integration possible	Low risk of premature phase change	Simple design
Limitations	New operability challenges for phase-changing solids	Difficult to adapt to high delivery pressure; high wear of screw components	Large volumes of pressurizing gas needed; complex design	High wear of piston components

- Multiple options available for solids handling

Desorption

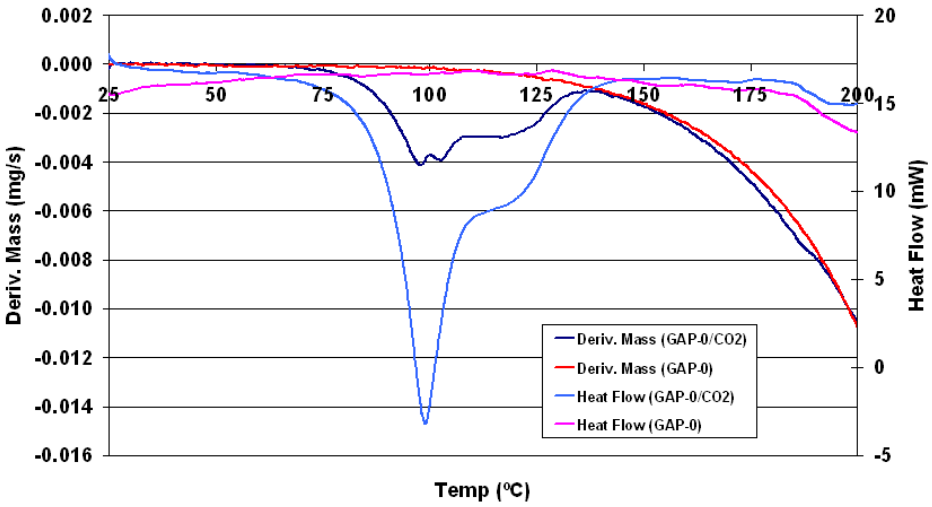


- Neat GAP-0 data
- >14% to <4%
- ~10% dynamic range



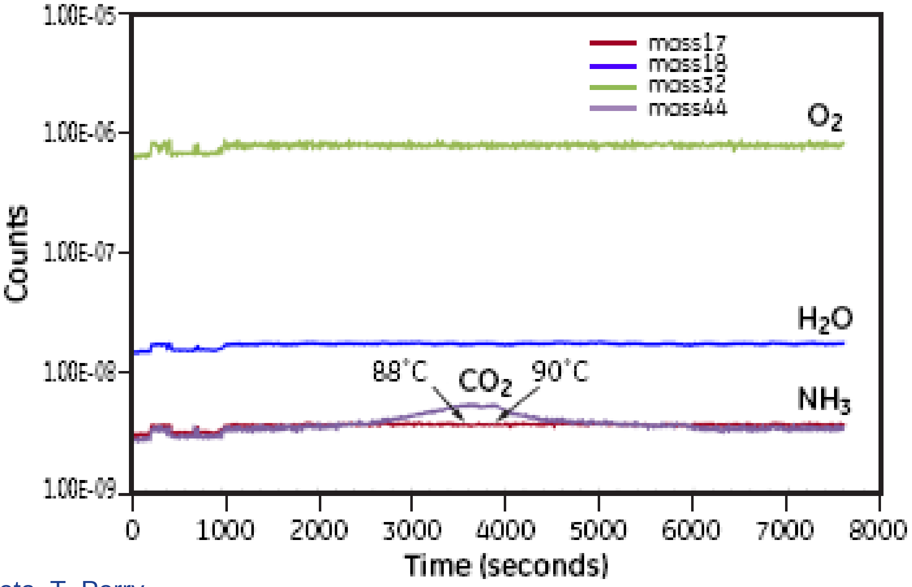
S. Genovese

Desorption

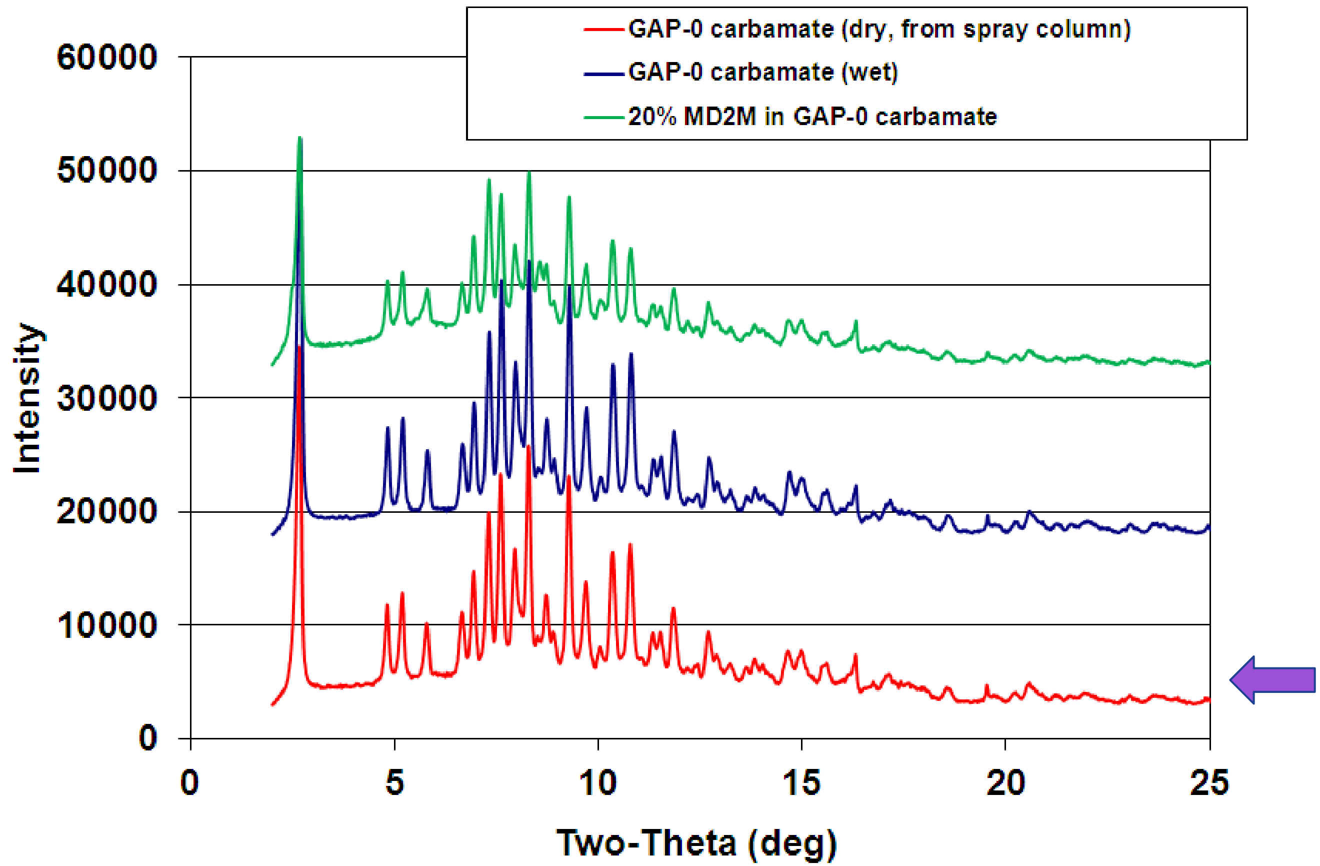


- TGA shows 3 events
- Onset at ~70 ºC
- Major loss 90-110 ºC
- DSC indicates 2 events
- Looking at desorption kinetics

- TGA/MS confirms only CO_2 loss
- No decomposition products
- Examining DSC/TGA profiles to differentiate phase changes from decarboxylation process



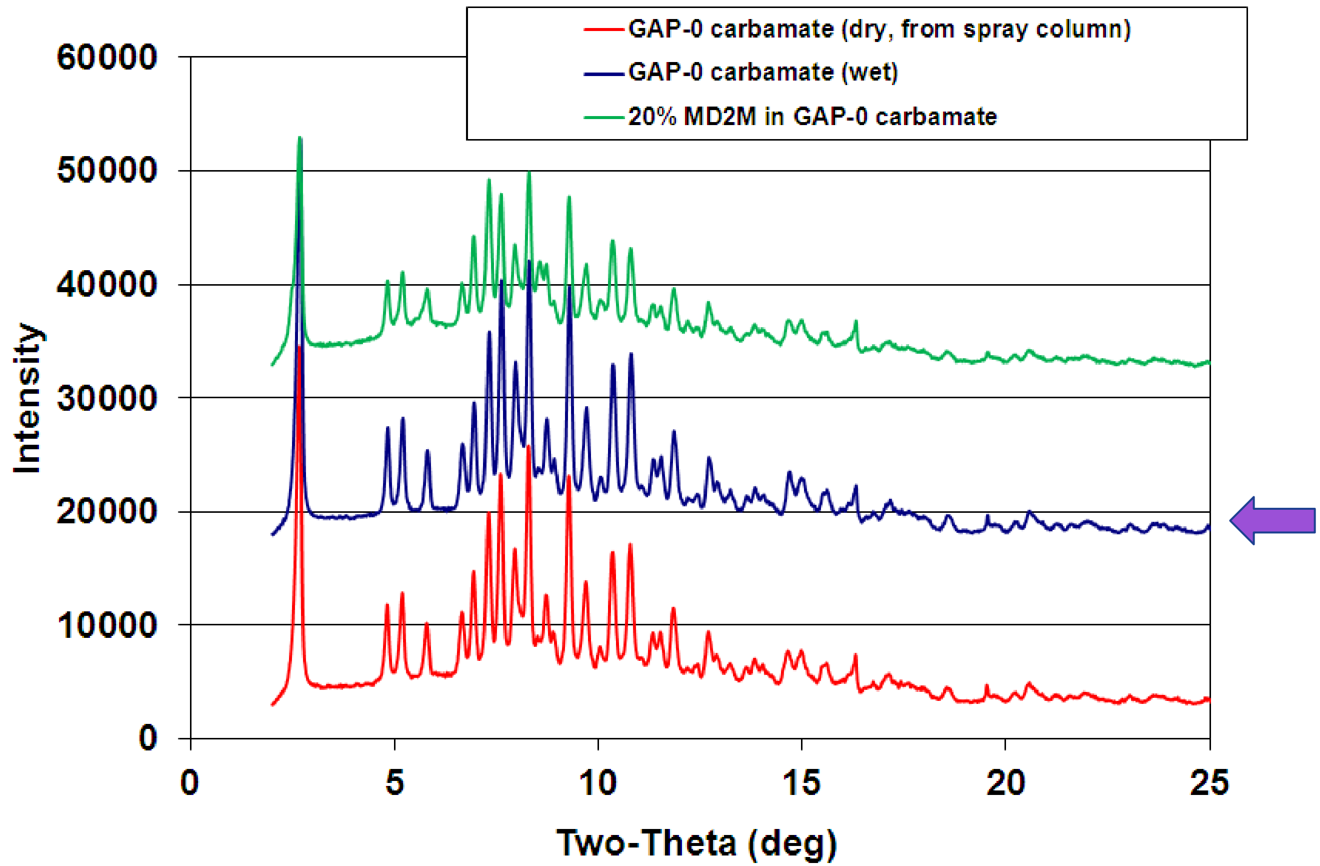
XRD



- GAP-0 carbamate is highly crystalline

B. Wood, C. Dosch, M. Meketa

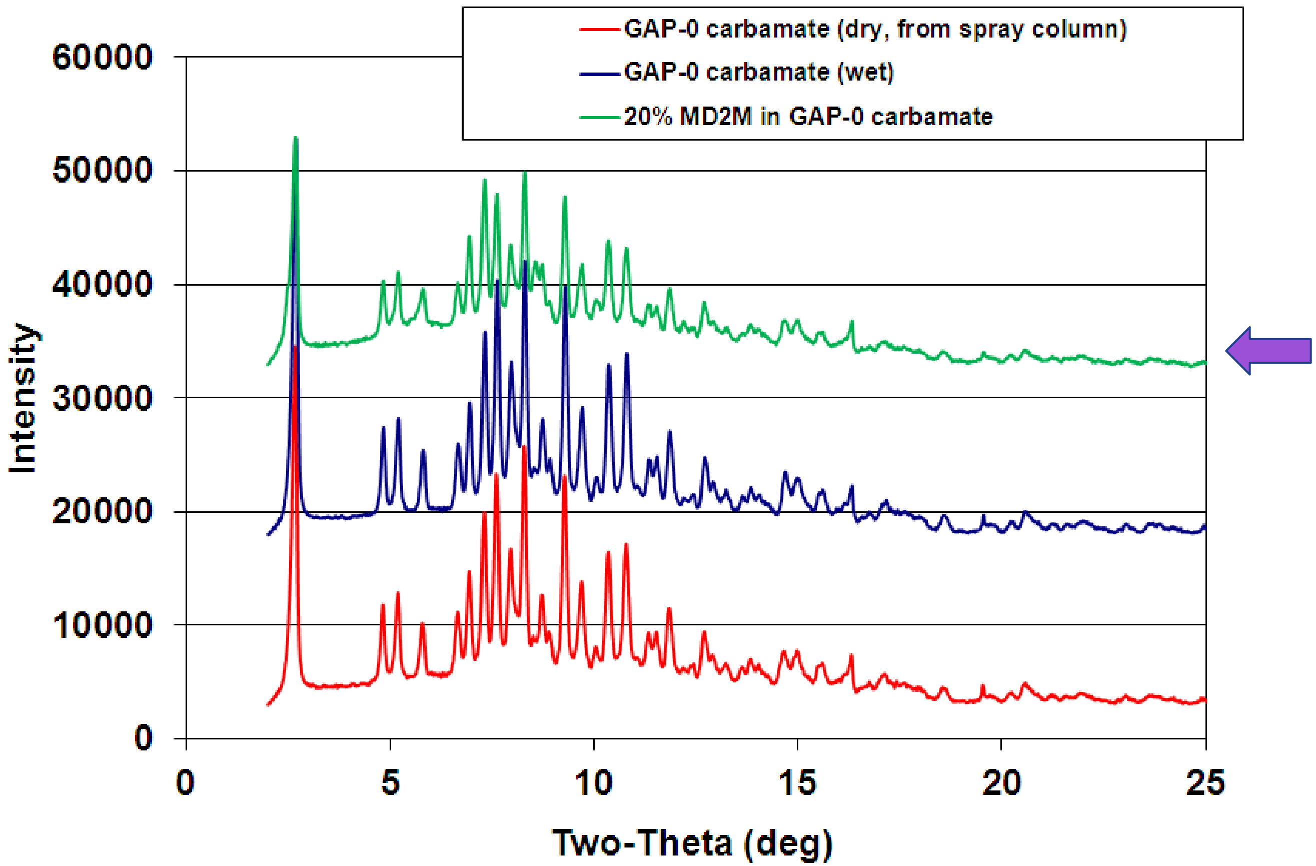
XRD



- GAP-0 carbamate is highly crystalline
- Water does not disrupt matrix

B. Wood, C. Dosch, M. Meketa

XRD

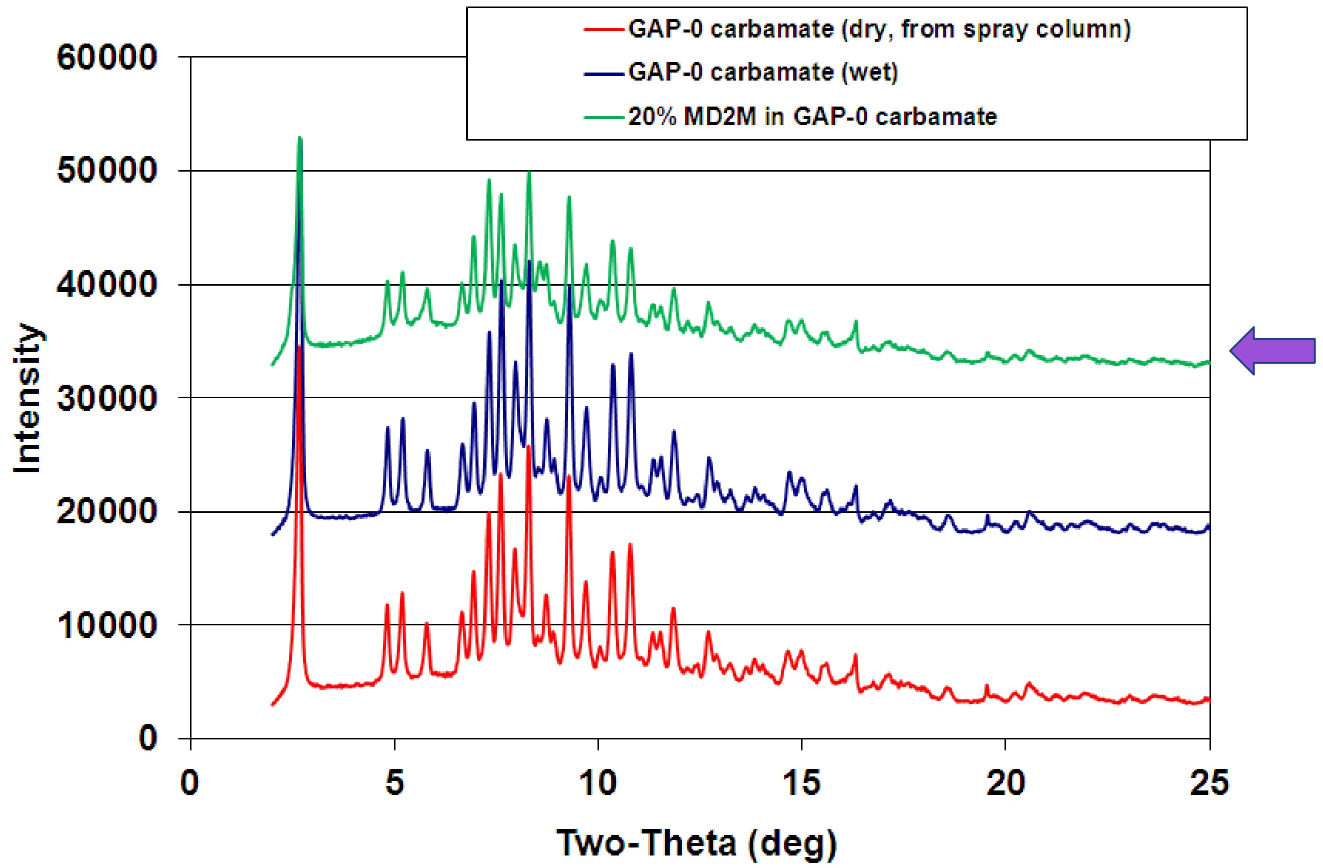


- GAP-0 carbamate is highly crystalline
- Water does not disrupt matrix
- Diluent does not affect XL structure

B. Wood, C. Dosch, M. Meketa

XRD

•How much does heat of crystallization affect ΔH_{rxn} ?



- GAP-0 carbamate is highly crystalline
- Water does not disrupt matrix
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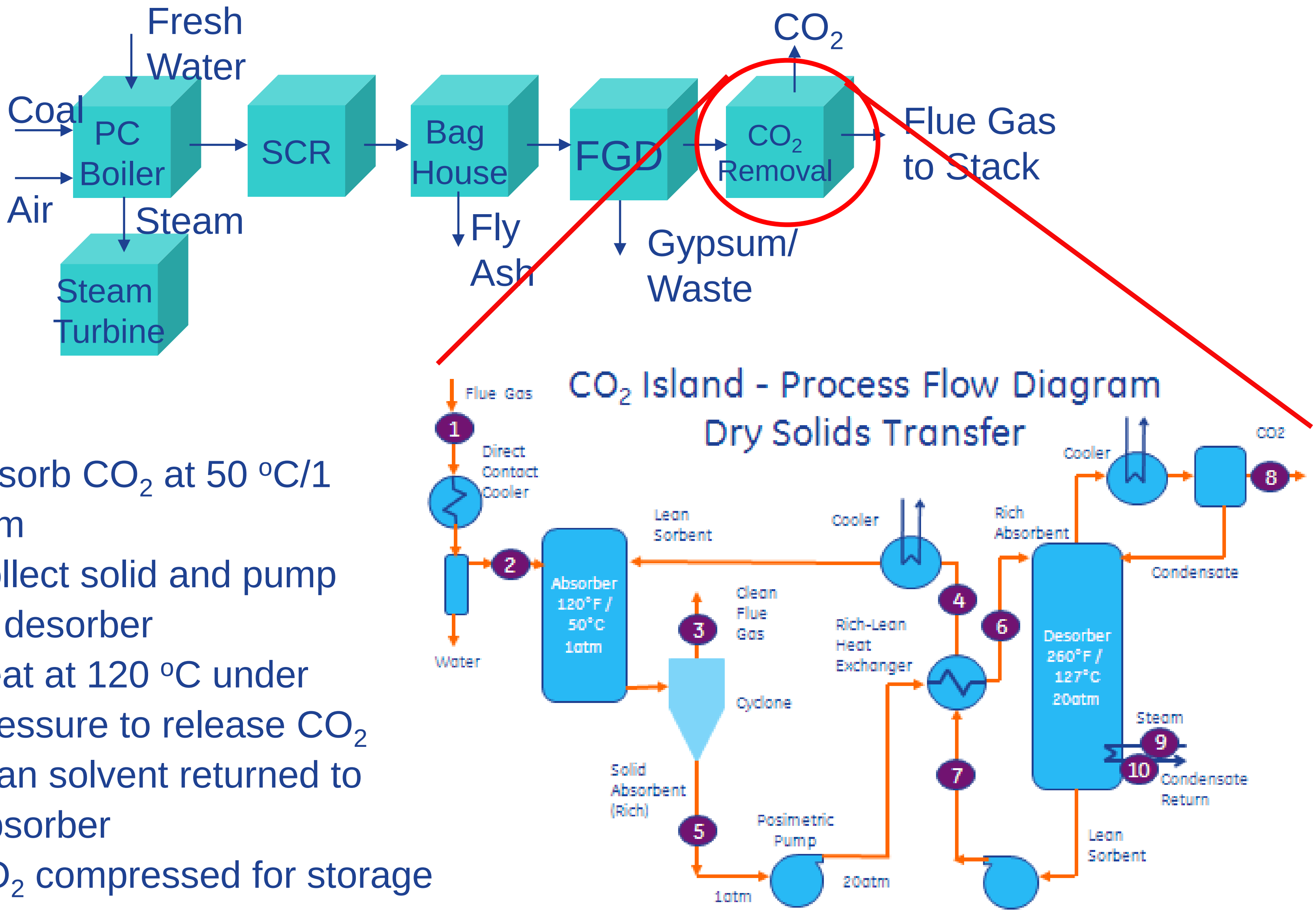
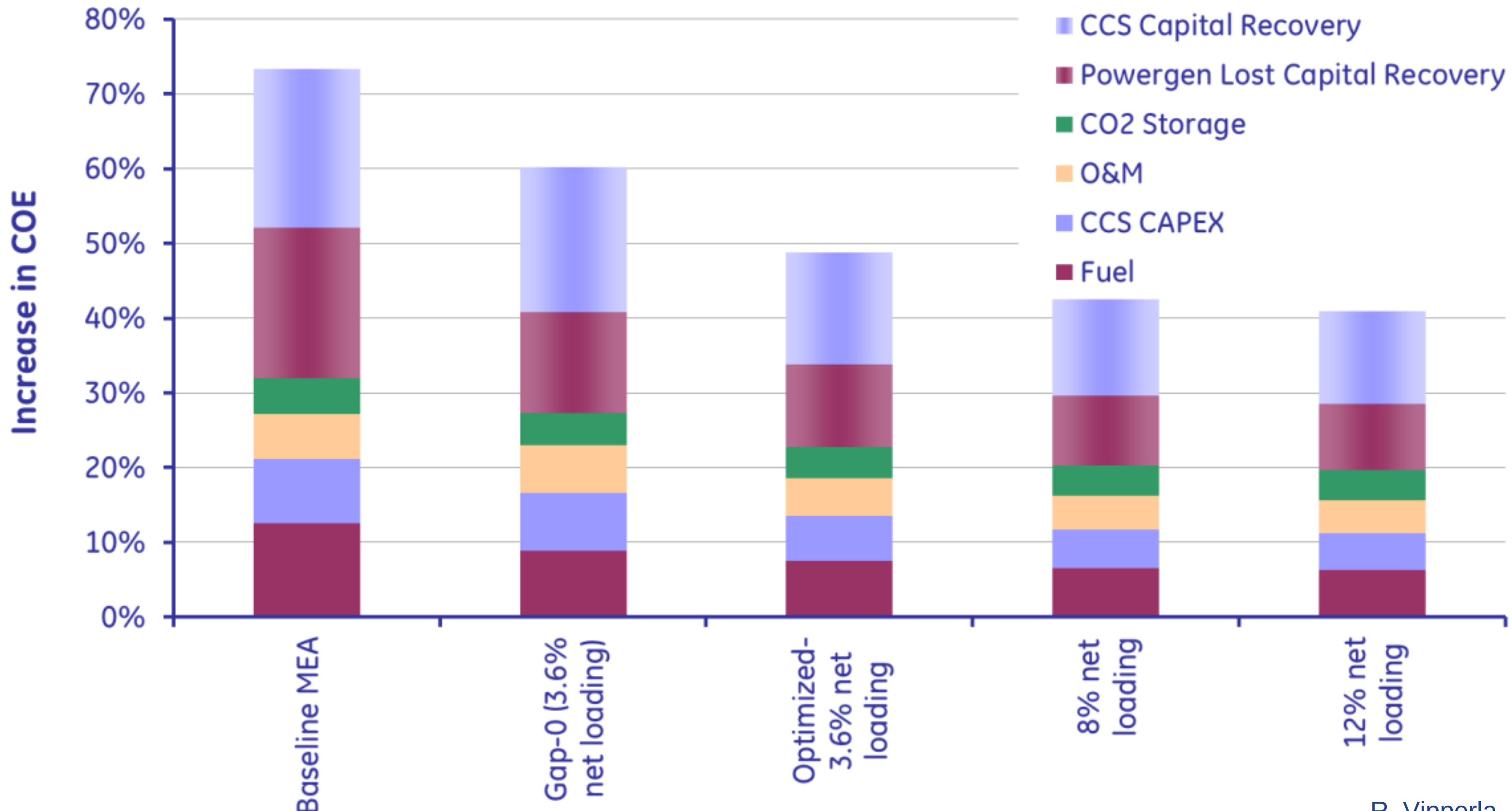
B. Wood, C. Dosch, M. Meketa

Process Schematic



- Absorb CO_2 at 50 ºC/1 atm
- Collect solid and pump to desorber
- Heat at 120 ºC under pressure to release CO_2
- Lean solvent returned to absorber
- CO_2 compressed for storage

Preliminary COE Waterfall



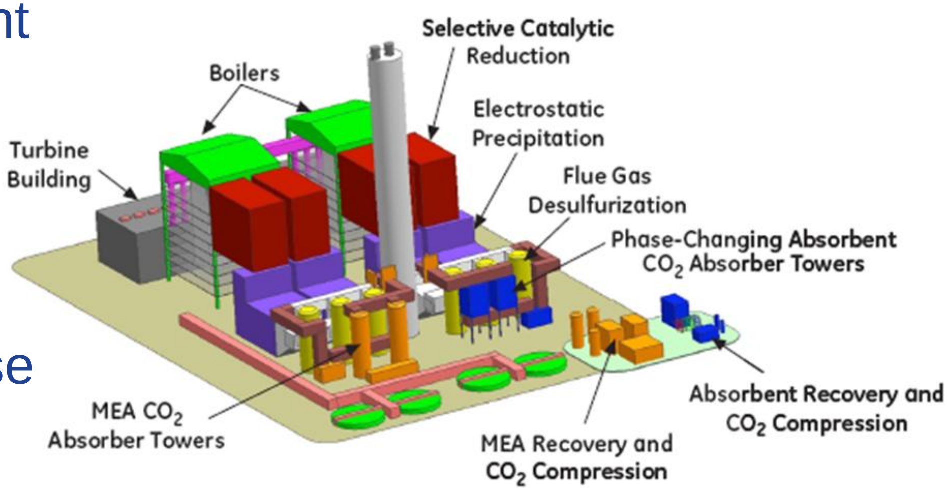
R. Vipperla

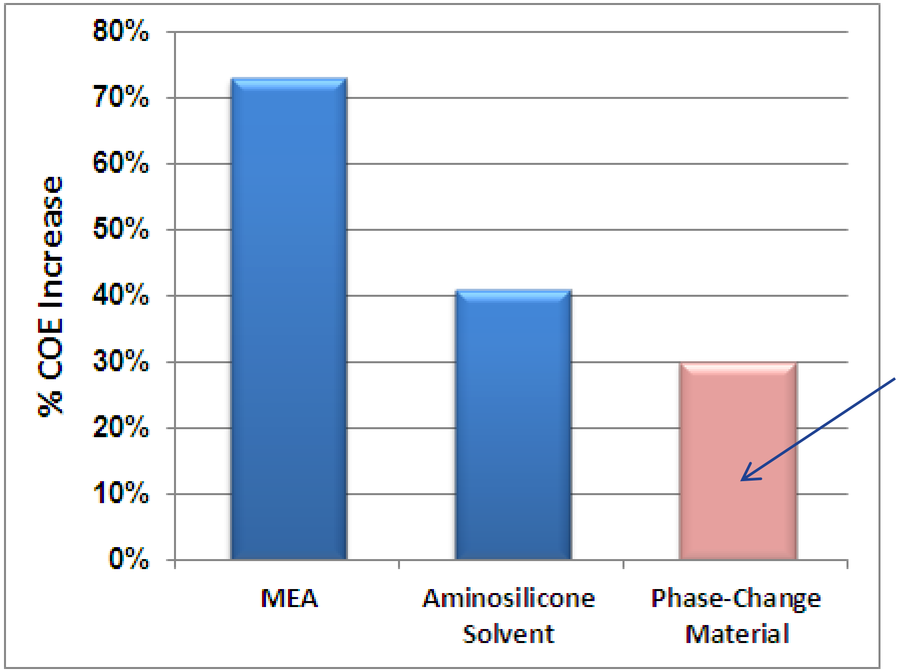
- Large savings with low water
- Higher net loading of CO_2 provides decrease COE
- Optimized plant operation (desorption, HX) offers savings

imagination at work

Plant Modeling and COE Calculations

- Elimination of water and co-solvent
- Increased CO_2 capture capacity
- Higher desorption pressure/temp
- Substantial decrease in energy use
- Smaller COE increase





Target for decreased COE

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Moving Forward

- Complete solvent development/down-selection
- Ratify action of stabilizers
- Finish unit operations designs
- Conclude construction of absorber, solids transfer and desorber units
- Confirm operation of unit ops
- Integrate unit operations into COE calculations
- Validate original premise/assumptions
- Acquire funding for scale-up process

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Thank you